23.2 Enthalpies of solution and hydration

Name: _____ Class: _____ Date: _____ **Total: 23 marks**

KEY WORDS enthalpy change of hydration 水合焓变 • enthalpy change of solution 溶解焓变 • enthalpy change 焓变 • lattice energy 晶格能

Objective

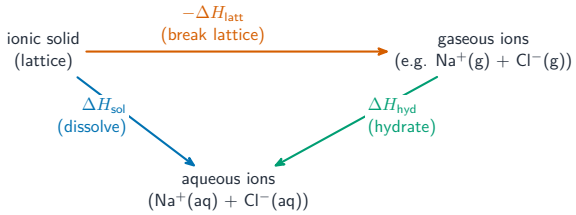
Build the skills to answer exam questions on **enthalpies of solution and hydration** — $\Delta H_{\mathbf{sol}}$ 溶解焓 and $\Delta H_{\mathbf{hyd}}$ 水合焓, the energy cycle, and the effect of ionic charge and radius.

You must be able to:

- define enthalpy of solution and enthalpy of hydration
- construct and use an energy cycle linking them with lattice energy
- explain the effect of ionic charge and radius on the magnitude of hydration enthalpy

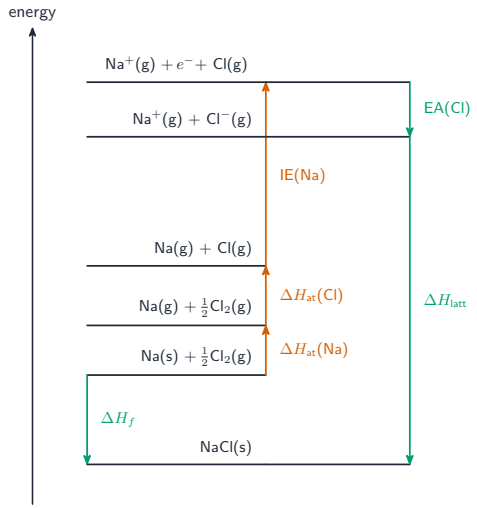
1 Worked examples

The dissolving cycle



$$\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$$

Dissolving = breaking the lattice ($-\Delta H_{latt}$) then hydrating the ions (ΔH_{hyd})



Lattice energy from a Born-Haber cycle

$$\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \sum \Delta H_{\text{hyd}}$$

- $\Delta H_{\mathbf{hyd}}$ — change when 1 mol of gaseous ions is dissolved in water (always −, water attracts the ion).
- $\Delta H_{\mathbf{sol}}$ — change when 1 mol of solute dissolves to form a solution.

Charge and radius

Hydration is **more exothermic** for ions with a **higher charge** and a **smaller radius** (higher charge density attracts the polar water more strongly).

2 Practice

2.1 Define **enthalpy change of hydration**. [2]

2.2 State **two** factors that make hydration of an ion more exothermic. [2]

3 Exam-style questions

3.1 Enthalpy of hydration is most exothermic for: [1]

- **A** a large, singly-charged ion
- **B** a small, highly-charged ion
- **C** a large, highly-charged ion
- **D** a neutral atom

3.2 Which equation correctly links the enthalpies? [1]

- **A** $\Delta H_{sol} = \Delta H_{latt} + \Delta H_{hyd}$
- **B** $\Delta H_{sol} = -\Delta H_{latt} + \Delta H_{hyd}$
- **C** $\Delta H_{sol} = \Delta H_{latt} - \Delta H_{hyd}$
- **D** $\Delta H_{sol} = -\Delta H_{hyd}$

3.3 For a salt, $\Delta H_{latt} = -780$ kJ mol^{-1} and the sum of the hydration enthalpies of its ions is -820 kJ mol^{-1}.

(a) Calculate the enthalpy change of solution. [2]

(b) State whether the salt dissolving is exothermic or endothermic. [1]

3.4 Explain why the hydration enthalpy of Mg^{2+} is more exothermic than that of Na^{+}. [2]

3.5 The table gives data for two Group 2 chlorides.

	$\Delta H^{\ominus}_{LE}$ / kJ mol^{-1}	$\Delta H^{\ominus}_{sol}$ / kJ mol^{-1}
$MgCl_2$	-2526	-155
$CaCl_2$	-2258	-83

$\Delta H^{\ominus}_{hyd}(Cl^-) = -364$ kJ mol^{-1}.

(a) Draw the energy cycle linking lattice enthalpy, enthalpy of solution and the enthalpies of hydration, and use it to calculate $\Delta H^{\ominus}_{hyd}(Mg^{2+})$. [5]

(b) Explain why $\Delta H^{\ominus}_{hyd}(Mg^{2+})$ is more exothermic than $\Delta H^{\ominus}_{hyd}(Ca^{2+})$. [3]

(c) Both dissolvings are exothermic, yet the magnitudes are small compared with the individual terms. Explain why. [2]

(d) State one reason why a calculated lattice enthalpy from a purely ionic model may differ from the experimental value. [2]

Solutions

2.1 the enthalpy change when 1 mol of gaseous ions is dissolved in (a large amount of) water.

2.2 a higher ionic charge; a smaller ionic radius.

3.1 B. A small, highly-charged ion has the highest charge density, so the most exothermic hydration.

3.2 B. $\Delta H_{\text{sol}} = -\Delta H_{\text{latt}} + \Delta H_{\text{hyd}}$.

3.3 (a) $\Delta H_{\text{sol}} = -(-780) + (-820) = +780 - 820 = -40$ kJ mol^{-1}.
(b) exothermic.

3.4 Mg^{2+} has a higher charge and a smaller radius than Na^{+}, so a higher charge density that attracts the polar water molecules more strongly — more exothermic hydration.

3.5 (a) The cycle goes: solid $\rightarrow$ gaseous ions ($-\Delta H_{\text{LE}}$) $\rightarrow$ aqueous ions ($\sum \Delta H_{\text{hyd}}$), and directly solid $\rightarrow$ aqueous ions (ΔH_{sol}). So $\Delta H_{\text{sol}} = -\Delta H_{\text{LE}} + \Delta H_{\text{hyd}}(Mg^{2+}) + 2\Delta H_{\text{hyd}}(Cl^{-})$; $-155 = 2526 + \Delta H_{\text{hyd}}(Mg^{2+}) + 2(-364)$; $\Delta H_{\text{hyd}}(Mg^{2+}) = -155 - 2526 + 728 = -1953$ kJ mol^{-1}.
(b) Mg^{2+} is the smaller ion but carries the same 2+ charge, so it has the greater charge density; it attracts the $\delta-$ oxygen of the water molecules more strongly, releasing more energy per mole.
(c) ΔH_{sol} is the small **difference** between two very large opposing terms — the energy needed to pull the lattice apart and the energy released on hydration; they nearly cancel, so the net value is small.
(d) The purely ionic model assumes perfect spheres with no covalent character; a small, highly charged cation polarises a large anion, giving some covalent character and a larger experimental lattice enthalpy than calculated.